BACKGROUND OF THE INVENTION

Throughout the world there is increasing interest in converting renewable biomass to usable products such as ethanol.

Biomass contains two basic constituents, carbohydrates and lignin. The carbohydrate content of the biomass contains cellulose and hemicellulose. Both cellulose and hemicellulose may be converted to sugars of glucose and xylose. Fermentation converts glucose and xylose to ethanol using enzymes produced by microorganisms revealed in U.S. patent No. 5,789,210. Control of nutrients, pH, temperature, sugar concentration, and microorganism concentration all affect rate of fermentation to form ethanol. When ethanol concentration reaches above about 6 to 12%, ethanol concentration is lethal to the microorganisms employed for fermentation.
To reduce ethanol concentration within broth employed for fermentation and maintain activity of microorganisms, extraction of ethanol from the broth by solvents non-toxic to microorganisms, is disclosed in U.S. patents No.s 5,110,319, 4,865,973 and No. 4,517,298. The operations disclosed require energy for vaporization of ethanol and subsequent condensation to produce liquid ethanol.

It is therefore an object of this invention to obviate many of the limitations or disadvantages of the prior art .

The present concern of this invention is to prevent concentration of ethanol within a broth from reaching a concentration of ethanol lethal to microorganisms employed for fermentation.

An object of this invention is to remove ethanol contained within a broth by providing carbon dioxide to the broth to humidifying ethanol within the carbon dioxide.

An additional object is to substantially remove ethanol from ethanol humidified by carbon dioxide and provide carbon dioxide for subsequent humidification of ethanol.

Still another object of this invention is to vaporize ethanol within broth from heat from fermentation

Yet another object of this invention is to substantially maintain sugars and microorganisms within the fermentation vessel as required to continue fermentation.

Additionally an object of this invention is to substantially maintain volume of broth within the fermentation vessel

With the above and other objects in view, this invention relates to the novel features and alternatives and combinations presently described in the brief description of the *invention.*

THEORETICAL BACKGROUND OF THE INVENTION

The principles applied herein employ Dalton's law and Raoult's law. Dalton's law of partial pressure may be expressed mathematically as $P = p_A + p_B +$ where p_A and p_B are the partial pressures of vapors A and B respectively and P is the total pressure.

For only A and B, $P = p_A + p_B$, and the mole ratio of B to A is $p_B / p_A = p_B / P - p_B$.

The weight ratio of A/ B is $p_B / P - p_B$ (molecular weight of B)/(average molecular weight of $P - p_B$). This is the equation used for humidity calculations when A is a gas and B is the vapor humidified. Raoult's law of partial pressure may be expressed mathematically as

p solvent = p^o solvent (N) solvent where p solvent is the partial vapor pressure of the solvent, p^o solvent = the vapor pressure of the solvent times the mole fraction N of the solvent within a solution. Applying Raoult's law, let N = 0.1 (the mole fraction of ethanol within a fermentation broth) and p^o ethanol at a temperature 0f 100° F, taking the partial vapor pressure at about 2.5 psia then p ethanol = 0.1 (2.5) psia = 0.25 psia.

The molecular weight of ethanol = 46 and carbon dioxide has a molecular weight = 44.

Applying the equation used for humidity, and let P = 15 psia for a total pressure of humidified Carbon Dioxide, the weight ratio of ethanol/ carbon dioxide is 0.25/15-0.25 (46/44) = 0.018 lb. of ethanol /lb. of carbon dioxide. Accordingly a fermentation broth can have ethanol transferred by co-mingling carbon dioxide with the fermentation broth to form carbon dioxide humidified with ethanol. Humidified carbon dioxide by ethanol from fermentation is scrubbed by water to produce carbon dioxide substantially free of ethanol and water containing dissolved ethanol, disclosed by R.N. Shreve, Chemical Process Industries, 1956, page 130.

Raoult's law predicts that any volatile compound within a fermentation broth will form a partial vapor pressure of the volatile compound depending on the vapor pressure and mole fraction of the volatile compound within the fermentation broth. The equation used for humidity allows,that when a gas is humidified, the humidified gas may contain any partial vapor pressure of a volatile compound. Thus if the humidified carbon dioxide contains a partial vapor pressure of a volatile compound contained within the fermentation broth of the same partial vapor pressure of the same volatile compound then further humidification of the volatile compound such as water will not occur. Carbon dioxide, saturated within water, forms carbonic acid of pH level about 4; Therefore broth during fermentation is substantially maintained at a constant pH level.

The reverse of humidification is dehumidification. These procedures occur with simultaneous heat and mass transfer. Humidification of ethanol to provide a vapor within a gas requires heat of vaporization derived from heat formed during fermentation of sugars. Sugars, capable of fermentation within which ethanol and carbon dioxide are produced, are selected from the group consisting of glucose, xylose and mixtures thereof. Dehumidification of ethanol transfers ethanol vapors from a gas to a phase of a difference in ethanol partial pressure acquiring heat of vaporization of ethanol within the process to provide heat to the phase and consequently the sensible heat of the phase. Fermentation evolves heat as disclosed by R.N. Shreve, *op.cit.* pages 672-673. Ethanol vapor required to humidify ethanol is accordingly supplied by heat evolved during fermentation.

Microorganisms contained within broth will ultimately lose activity for fermentation and must be removed and replaced by active microorganisms. Enzymes produced from microorganisms are proteins that can be coagulated and precipitated by heat or chemical compounds as established by Hill and Kelley within Organic Chemistry, 1943, pages 442-443. Therefore broth containing diminish activity of microorganisms and enzymes can be heated to produce insoluble sludge within broth.

A ternary system created by benzene to form a low boiling point azeotrope with ethanol, water and benzene is employed within distillation columns to produce anhydrous ethanol as described by R.N. Shreve, *op.cit.,* page 679. Analogously gasoline, ethanol and water form a low boiling point azeotrope which is utilized within distillation columns to produce anhydrous gasoline containing ethanol. Hydrocarbon compounds often found within gasoline are heptane and hexane. Azeotropes of these hydrocarbons, ethanol and water are listed in Handbook of Chemistry and Physics, 56th Edition, page D-42.

Salts subjected to water to form hydrates include calcium sulfate and aluminum sulfate as disclosed by R.N. Shreve, *op.cit.* page, 218 and page 436. Accordingly gasoline containing ethanol and water can be employed to produce anhydrous gasoline by forming a hydrate within the gasoline containing water followed by separation of the hydrate to yield anhydrous gasohol. For additional information, review F. Daniels, Outlines of Physical Chemistry and G. G. Brown, et al., Unit Operations.

BRIEF DESCRIPTION OF THE INVENTION

The present invention in its broadest aspect, provides a method to withdraw ethanol from a fermented broth contained within a fermentation vessel. The preferred embodiment of the method employs carbon dioxide, supplied to the fermentation vessel, to humidify ethanol. Ethanol from the broth is transmitted to and co-mingled with carbon dioxide to humidify the carbon dioxide. The carbon dioxide containing humidified ethanol and carbon dioxide produced by fermentation is removed from the fermentation vessel and substantially separated from the ethanol. Carbon dioxide, substantially separated from the ethanol, is then purged of carbon dioxide to substantially equal carbon dioxide formed from fermentation. The carbon dioxide is then recycled to humidify additional ethanol within fermented broth. Consequently the fermented broth provides ethanol to humidifiy carbon dioxide which is then separated from the fermentation vessel.

Characteristics of the invention include;

A fermentation vessel is provided for fermentation of sugars to form ethanol and carbon dioxide from a fermentation broth contained within a fermentation vessel.

Carbon dioxide is provided to the fermentation vessel and co-mingled with the fermentation broth.

Ethanol and other volatile components contained within the fermentation broth are humidified by carbon dioxide and removed from the fermentation vessel. Depending on the composition of the fermented broth, volatiles contained within the carbon dioxide can be of several types including aldehydes, alcohols, esters and acids.. Carbon dioxide and ethanol produced from fermentation is substantially removed from the carbon dioxide.

Fermentation produces heat, that is substantially proportional to ethanol produced, that is employed to evaporate ethanol.

Microorganisms, required for fermentation, are replenished within the fermentation vessel to maintain their activity.

Sludge, sugars, nutrients and microorganisms are removed from the fermentation vessel as required to maintain the volume of the fermentation broth.

Withdrawal of ethanol from fermentation broth to humidify carbon dioxide is utilized to produce an ethanol concentration within the broth of about 6% to about 12%.

BRIEF DESCRIPTION OF THE DRAWINGS

The features that are considered characteristic of this invention are set forth within the appended claims. This invention, however, both as to its origination and method of operations as well as additional advantages will best be understood from the following description when read in conjunction with the accompanying drawings in which:

FIG. 1 is a flow sheet denoting the invention as set forth in the appended claims.

FIG. 2 is a flow sheet denoting an alternate method for substantially separating ethanol from ethanol humidified carbon dioxide.

FIG. 3 is a flow sheet denoting a method to substantially separate sludge from broth contained within broth and sludge.

FIG. 4 is a flow sheet denoting a method to substantially absorb ethanol humidified carbon dioxide with gasoline to form gasohol.

FIG. 5 is a flow sheet denoting an alternate method to substantially absorb ethanol humidified carbon dioxide with gasoline to form gasohol.

FIG. 6 is a flow sheet denoting a method to substantially extract ethanol contained within water with gasoline to form gasohol.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred embodiment of the present invention, a fermented broth is co-mingled with carbon dioxide, forming two phases for humidifying the carbon dioxide with ethanol from the fermented broth. The operating temperature range for fermentation is about 30°C to about 35°C.

The flow diagram of **Fig. 1** illustrates the general preferred embodiment of the present invention. In the diagram, rectangles represent stages, operations or functions of the present invention and not necessarily separate components. Arrows indicate direction of flow of material in the method.

Referring to **Fig. 1,** a mixture of microorganisms, nutrients and sugars **10** is provided to a fermentation vessel **12,** to form a fermentation broth. Upon fermentation, the broth forms ethanol and carbon dioxide which is transmitted to provided carbon dioxide **16,** devoid of released carbon dioxide **16A**. Released carbon dioxide **16A** removes the quantity of carbon dioxide formed from fermentation. The humidification and removal of formed ethanol contained within humidified

carbon dioxide **18** is transported to ethanol absorption **20** which dissolves ethanol within a solvent **24** to form dissolved ethanol **22** which is then transmitted to heat exchanger **26** which, forms heated ethanol within solvent **28,** and is then transported to distillation **30** to distill ethanol **32** from the solvent **34** for transfer to heat exchanger **26.** Solvent **34,** produced from distillation **30,** is then transmitted to heat exchanger **26** which transfers heat to dissolved ethanol **22** to establish heated ethanol dissolved within solvent **28** for transfer to distillation **30** which provides solvent **24** for employment within ethanol absorption **20.** Solvent **34** must be capable of dissolving ethanol and capable of separation of ethanol from distillation **30** to provide solvent substantially free of ethanol. The method will withdraw the ethanol humidified carbon dioxide, containing carbon dioxide from the fermentation, **18** from the fermentation vessel. Fermentation sludge and broth **14**, removed from the fermentation vessel, is available for further treatment. The method depicted in **Fig. 1** employs humidification for transmitting ethanol from fermented broth to carbon dioxide. Controlled flow rate of gaseous carbon dioxide is provided to maintain ethanol concentration within the broth. The humidified carbon dioxide may contain various volatile compounds from the fermented broth. The method can be operated either batch ways or by continuous operation. Microorganisms within the fermentation broth become inacive and are removed from the fermentation vessel as sludge and broth **14.** The fermentation vessel **12**, utilized in plug flow operation, will segregate microorganisms of reduced inactivity for removal from the fermentation vessel as sludge and broth **14.** The mixture **10,** containing microorganisms, nutrients and sugars can be a separate solution of microorganisms and a solution of nutrients and a solution of sugars combined within the fermentation vessel or a single solution containing microorganisms, nutrients and sugars. The sugars, capable of fermentation to produce ethanol and carbon dioxide, may consist of the group of carbohydrates which include glucose and xylose. Energy formed from fermentation must be removed from the broth to maintain broth temperature. Removal of the energy is commonly accomplished by a heat exchanger, not depicted in **Fig. 1,** to maintain substantially isothermal broth. Carbon dioxide **16,** combined with carbon dioxide from fermentation, will percolate upward within fermentation vessel **12** for removal of ethanol humidified carbon dioxide **18.** It is assumed that counter flow of carbon dioxide **16** is supplied from the lower end of the fermentation vessel **12** to remove ethanol humidified carbon dioxide **18.**

Ethanol absorption **20,** from ethanol humidified carbon dioxide **18,** is ordinarily a scrubbing tower supplied by a solvent to dissolve ethanol within a solvent to remove ethanol and form carbon dioxide **16.** Microorganisms within the fermentation broth likely contain or include yeasts.

Referring to **Fig. 2,** a mixture of microorganisms, nutrients and sugars **10** is provided to a fermentation vessel **12,** to form a fermentation broth. Upon fermentation, the broth forms ethanol and carbon dioxide which is transmitted to the provided carbon dioxide **16,** devoid of released carbon dioxide **16A**. Released carbon dioxide **16A** removes the quantity of carbon dioxide formed from fermentation. The humidification and removal of formed ethanol contained within humidified carbon dioxide **18** is transported to ethanol absorption **20** which dissolves ethanol within water **44** to form dissolved ethanol **46** and is then transmitted to heat exchanger **26** which is then transported to distillation **38** to distill ethanol **40** from the water **42** for transfer to heat exchanger **26.** Water **42** produced from distillation **38** is then transmitted to heat exchanger **26** which transfers heat to dissolved ethanol **46** is establish heated ethanol dissolved within water **36** for transfer to distillation **38** and produces water **44** for employment within ethanol absorption **20.** The method will withdraw, from the fermentation vessel, ethanol humidified carbon dioxide **18** containing carbon dioxide from fermentation. Fermentation sludge and fermentation broth **14,** removed from the fermentation vessel, is available for further treatment. Water **44** generally contains ethanol not stripped within distillation **38.** Water **44A** is added to water **44** to provide makeup for water removed within distilled ethanol **48**. Ethanol absorption **20,** from ethanol humidified carbon dioxide **18,** is routinely a scrubbing tower supplied by water to dissolve ethanol within water to remove ethanol and form carbon dioxide **16.**

Referring to **Fig. 3,** broth and sludge **14** is transmitted to separate stage **56** which functions to separate solution **10A** from sludge **58.** Separate stage **56,** for example, can be supplied by a microfiltration filter or a settling tank. Broth **10A** after separation is then recycled to the fermentation vessel **12** to regulate fermentation broth and combine with mixture **10.** Broth and sludge **14** may be concentrated by microfiltration to reduce volume to separation stage **56.** Carbon dioxide **16A,** formed within separate stage **56,** during fermentation is combined with humidified carbon dioxide **18.** A mixture of microorganisms within the broth has been accordingly rendered insoluble.

Referring to **Fig. 4** ethanol humidified carbon dioxide **18** is subjected to ethanol absorption **60** by gasoline **62** to dissolve ethanol and form gasohol **64** and gasoline humidified carbon dioxide **66**

which is transmitted to gasoline adsorption **68** to substantially adsorb gasoline from carbon dioxide and produce carbon dioxide **16A** substantially free of gasoline.
Gasoline adsorption **68** becomes gasoline absorbate **68** and is heated by heat **70** to form vapor **18A.** Adsorption media contained within gasoline adsorption **68** is reused to adsorb additional gasoline from gasoline humidified carbon dioxide **66.**

Referring to **Fig. 5** ethanol humidified carbon dioxide **18** is subjected to ethanol absorption **72** by gasoline **74** for absorption of ethanol to form gasohol **78** for transportation to distill stage **80** to form vapor **84** and gasohol **82.** Vapor **84** is condensed in condense stage **86** to form a condensate **88** separated into upper phase **78A** and a lower phase **92** in phase forming stage **90.** The upper phase **78A** is combined with gasohol **78.** The lower phase **92** is transfered to distill stage **94** to produce vapor **98** and raffinate **96.** Accordingly dehydrated gasohol **82** is produced. Raffinate **96.** composed fundamentally of water is available for process water. Undisclosed within **Fig. 5,** gasoline humidified carbon dioxide **76** is subjected to additional treatment to free gasoline from carbon dioxide.

Referring to **Fig. 6**,. water containing ethanol **46** is extracted by extract stage **100** with gasoline **102**, to produce gasoline and water **106**, and to produce an extractate **104** containing extracted ethanol. Gasoline and water **106** are distilled within distill stage **114** to produce raffinate **116** and vapor **118** to be condensed within condense stage **120** to produce condensate **122** to be combined with water containing ethanol **46.** Extracxtate **104** is dehydrated within dehydrate stage **106** from salt **108** to produce gasohol **110** and a hydrate **112**. Raffinate **116** is commonly used to supply water **44** and water **44A**. Dehydration of gasohol, containing extracted ethanol, may be performed by a salt to form a hydrate or a concentrated solution such as calcium chloride or a dehydration desiccant, as an example, silica gel. Undisclosed within **Fig. 6,** Hydrate **112** is subjected to heat to produce a vapor for combination with vapor **118** and a desiccant for combination with salt **108.** Accordingly, dehydrated gasohol **110** is produced.

The following examples are set forth to illustrate more clearly the principles and practice of the invention.

EXAMPLE 1

To demonstrate the method, 7 grams of Red Star yeast is dissolved within 50 cc of water to form a mixture. 10 grams of glucose is dissolved within 50 cc of water to form a separate mixture. Both mixtures are combined within a one quart jar, with stirring, and then covered to establish aerobic fermentation within the combined mixture. Fermentation, with occasional agitation, proceeds at room temperature until foaming and effervesce of carbon dioxide no longer emanates from the fermenting mixture. Fermentation is allowed to continue for 24 hours. The fermented mixture, thus formed, is allowed to settle to segregate sludge from the broth. The broth is decanted from the sludge to provide broth separated from the sludge.

EXAMPLE 2, PART 1

To illustrate a method for producing anhydrous gasohol, one pint of gasohol contained within a one quart jar, is brought to boil. The boiling point, not definite, was initially found to be about 50 degrees C. The gasohol following investigation was discarded.

EXAMPLE 2, PART 2

One pint of gasohol combined with a volume of water contained within a one quart jar, is stirred to saturate the gasohol with water and then decanted to separate saturated gasohol from the water.

EXAMPLE 2, PART 3

One pint of gasohol saturated with water, contained within a one quart jar, is brought to boil. The boiling point, not definite, initially was found to be about 40 degrees C. indicating a low boiling ternary vapor of water, ethanol and a component of gasoline to yield anhydrous gasohol.
The gasohol following investigation was discarded.